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Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{S}-\text{Si}) = 0.002\text{ \AA}$
 R factor = 0.020
 wR factor = 0.038
Data-to-parameter ratio = 21.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Samarium chloride sulfide thiosilicate,
 $\text{Sm}_3\text{ClS}_2[\text{SiS}_4]$

Dominant in the structure of the title compound are two crystallographically different Si positions forming almost undistorted isolated $[\text{SiS}_4]^{4-}$ tetrahedra and four crystallographically different Sm positions with coordination numbers seven and eight. The thiosilicate is isotypic with $\text{Nd}_3\text{ClS}_2[\text{SiS}_4]$ [Hatscher & Urland (2002*d*), *Mater. Res. Bull.* In the press].

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Comment

The structures of compounds in the system of lanthanide, sulfide, silicon and halide have been one of our focuses over the last two years. Up to now, the following homologue groups have been published: the lanthanide iodide thiosilicates $\text{Ln}_3\text{I}[\text{SiS}_4]_2$ ($\text{Ln} = \text{La}-\text{Nd}, \text{Sm}$ and Tb) (Gauthier *et al.*, 1998*a,b*; Hatscher & Urland, 2001, 2002*c*), the lanthanide bromide thiosilicates $\text{Ln}_3\text{Br}[\text{SiS}_4]_2$ ($\text{Ln} = \text{La}-\text{Nd}, \text{Sm}$ and Gd) (Hatscher & Urland 2002*a*), and the lanthanide chloride thiosilicates $\text{Ln}_3\text{Cl}[\text{SiS}_4]_2$ ($\text{Ln} = \text{La}-\text{Pr}$) (Hatscher & Urland, 2002*b*), all crystallizing in the monoclinic space group $C2/c$. These compounds are isotypic with the so called A-type of the lanthanide chloride oxosilicates, first discovered by Gravaureau *et al.* (1988). With $\text{Nd}_3\text{ClS}_2[\text{SiS}_4]$ (Hatscher & Urland, 2002*d*), a new compound in this system was published with no oxo analogue so far known. We now present the heavier homologue, *viz.* $\text{Sm}_3\text{ClS}_2[\text{SiS}_4]$.

$\text{Sm}_3\text{ClS}_2[\text{SiS}_4]$ crystallizes in the orthorhombic space group $Pnma$. The structure displays two independent crystallographic positions of Si, and four different Sm positions. The Si atoms are surrounded by four sulfide ions each, forming

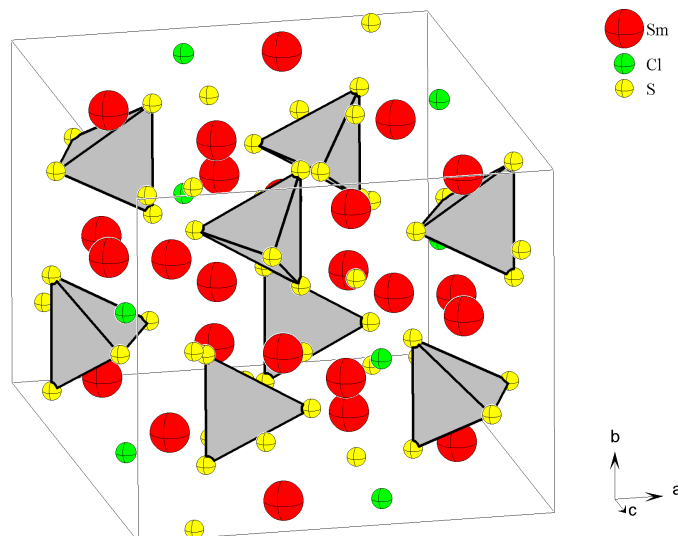


Figure 1
View of the crystal structure of $\text{Sm}_3\text{ClS}_2[\text{SiS}_4]$. The Si atoms are hidden in SiS_4 tetrahedra.

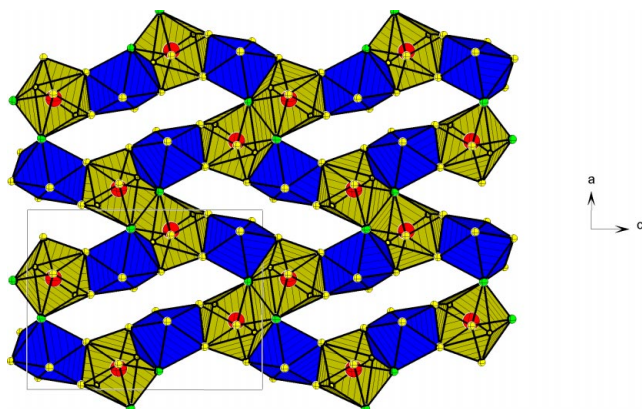


Figure 2
View, along [010], of the framework made up by Sm1 and Sm4 polyhedra. The Sm1 polyhedra are yellow and the Sm4 polyhedra blue.

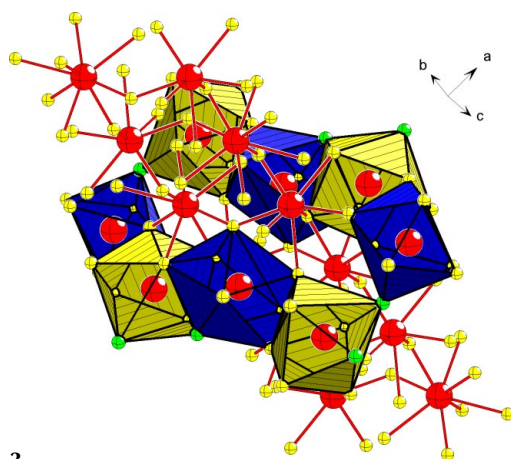


Figure 3
View of a ring of Sm1 (yellow) and Sm4 (blue) polyhedra with the double string of Sm2 and Sm3.

almost undistorted SiS_4 tetrahedra, which are isolated in the structure, as is usual for the lanthanide thiosilicates (Fig. 1). A common structural feature of the halogenide thiosilicates of the lanthanides is the formation of a chain of halogen atoms through the structure. Whereas in the homologues of the lanthanide chloride oxosilicates these tunnels are along the c axis, in the case of the title compound they are found along [010]. As in $\text{Ln}_3\text{X}[\text{SiS}_4]_2$ ($X = \text{Cl}, \text{Br}$ and I), the X atom shows a coordination of three lanthanide atoms. However, in the lanthanide halide thiosilicates of the type $\text{Ln}_3\text{X}[\text{SiS}_4]_2$, they form an isosceles triangle, whereas in the $\text{Ln}_3\text{ClS}_2[\text{SiS}_4]$ compounds a heavily distorted triangle is found. The Cl atoms are shifted out of the plane of the samarium ions. The weak fixation of the anion in the triangle of cations leads to the enlargement of the U_{22} displacement parameter along the direction of the chain. The Sm1, Sm2 and Sm4 ions are coordinated by eight anions, Sm3 by seven. The polyhedron surrounding Sm1 is made up by six sulfides and two chlorides, and the one around Sm4 by seven sulfides and one chloride. The others have only sulfide ligands. The dominant connection motifs are channels made up by Sm1 and Sm4 elements along [001]. These channels show alternating polyhedra of Sm1 and Sm4, each connected *via* edges (Fig. 2). In the space in the

centre, double strings of corner-sharing Sm2 and Sm3-polyhedra can be found (Fig. 3).

Experimental

Single crystals of the title compound were prepared from the elements. Samarium metal chips (StremChem, 99.9%), sulfur powder (Aldrich, 99.98%), silicon powder (Merck, >99%), and chlorine gas (Riedel-de Haën, >99%) were added to a quartz glass tube in a molar ratio of 1:2:0.3:~0.3. The ampoule was evacuated, sealed, and heated for 10 d in a two-zone furnace with its ends held at temperatures of 1273 and 1073 K. After cooling, a few air-stable orange crystals were obtained.

Crystal data

$\text{Sm}_3\text{ClS}_2(\text{SiS}_4)$
 $M_r = 706.95$
Orthorhombic, $Pnma$
 $a = 12.300$ (2) Å
 $b = 10.290$ (2) Å
 $c = 16.061$ (3) Å
 $V = 2032.8$ (7) Å³
 $Z = 8$
 $D_x = 4.620$ Mg m⁻³

Mo $K\alpha$ radiation
Cell parameters from 7998 reflections
 $\theta = 5.1$ – 56.1°
 $\mu = 18.65$ mm⁻¹
 $T = 293$ (2) K
Slab, orange
 $0.24 \times 0.18 \times 0.11$ mm

Data collection

Stoe IPDS diffractometer
 φ scans
Absorption correction: Gaussian
(X -RED; Stoe & Cie, 1998)
 $T_{\min} = 0.03$, $T_{\max} = 0.13$
32851 measured reflections
2446 independent reflections

2041 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.107$
 $\theta_{\max} = 28.3^\circ$
 $h = -16 \rightarrow 16$
 $k = -13 \rightarrow 13$
 $l = -21 \rightarrow 21$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.020$
 $wR(F^2) = 0.038$
 $S = 0.90$
2446 reflections
116 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0111P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.15$ e Å⁻³
 $\Delta\rho_{\min} = -1.47$ e Å⁻³
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00138 (3)

Table 1

Selected geometric parameters (Å).

Sm1—S5	2.7140 (11)	Sm3—S6	2.9305 (17)
Sm1—Cl1 ⁱ	2.8346 (12)	Sm3—S4 ^{ix}	2.9398 (12)
Sm1—S3	2.8646 (13)	Sm3—S4 ^x	2.9398 (12)
Sm1—Cl1 ⁱⁱ	2.8847 (14)	Sm4—S7 ⁱⁱⁱ	2.7109 (13)
Sm1—S7 ⁱⁱⁱ	2.9280 (13)	Sm4—S1	2.7331 (10)
Sm1—S8 ⁱⁱⁱ	2.9532 (7)	Sm4—Cl1 ⁱⁱ	2.7862 (12)
Sm1—S9	2.9572 (12)	Sm4—S6 ^{xi}	2.8904 (12)
Sm1—S4 ⁱⁱⁱ	3.0156 (13)	Sm4—S4 ^x	2.9704 (12)
Sm2—S1	2.8222 (18)	Sm4—S3 ^{xii}	3.0228 (13)
Sm2—S7 ⁱⁱⁱ	2.8663 (12)	Sm4—S2 ⁱⁱ	3.1223 (8)
Sm2—S7 ^{iv}	2.8663 (12)	Sm4—S5	3.3168 (14)
Sm2—S5	2.9223 (17)	Si1—S8	2.101 (2)
Sm2—S2	2.9279 (17)	Si1—S4	2.1109 (15)
Sm2—S3 ^v	2.9827 (12)	Si1—S4 ^{iv}	2.1109 (15)
Sm2—S3	2.9827 (12)	Si1—S6 ^{viii}	2.147 (2)
Sm2—S9 ^{vi}	3.1442 (18)	Si2—S2 ^{xiii}	2.100 (2)
Sm3—S1	2.7193 (16)	Si2—S3	2.1060 (16)
Sm3—S7 ^{vii}	2.7412 (12)	Si2—S3 ^v	2.1060 (15)
Sm3—S7 ^{viii}	2.7412 (12)	Si2—S9	2.109 (2)
Sm3—S8 ^{viii}	2.9107 (16)		

Symmetry codes: (i) $1+x, y, z$; (ii) $1-x, -y, 1-z$; (iii) $x, y-1, z$; (iv) $x, \frac{3}{2}-y, z$; (v) $x, \frac{1}{2}-y, z$; (vi) $x-\frac{1}{2}, y, \frac{3}{2}-z$; (vii) $1-x, y-\frac{1}{2}, 1-z$; (viii) $1-x, 1-y, 1-z$; (ix) $\frac{3}{2}-x, y-\frac{1}{2}, z-\frac{1}{2}$; (x) $\frac{3}{2}-x, 1-y, z-\frac{1}{2}$; (xi) $\frac{1}{2}+x, y, \frac{1}{2}-z$; (xii) $\frac{3}{2}-x, -y, z-\frac{1}{2}$; (xiii) $\frac{1}{2}+x, y, \frac{3}{2}-z$.

Tests in space groups with lower symmetry did not improve the residuals and led to no improvement of the structure solution. The maximum electron-density peak was located 1.27 Å from Sm4 and the minimum peak was 0.9 Å from Sm1.

Data collection: *IPDS Software* (Stoe & Cie, 1998); cell refinement: *IPDS Software*; data reduction: *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

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